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Supporting Information

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Heterogeneous Catalysis through Microcontact Printing**

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Supporting Information

Experimental Details

Reagents and General Methods. All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without purification. Dry solvents were obtained from a commercial DriSolv® solvent delivery system (EMD Chemicals). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (E. Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 500 (^{1}H: 500 MHz; ^{13}C: 126 MHz) or 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{19}F: 377 MHz) spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from the Me_4Si resonance as the internal standard for both ^{1}H and ^{13}C NMR spectroscopies and $CFCl_3$ as the internal standard for ^{19}F NMR spectroscopy. Electrospray ionization (ESI) mass spectra were measured on a Agilent LC/MS ion-trap mass spectrometer using 1 : 1 MeCN : H_2O as the mobile phase. Fast atom bombardment (FAB) mass spectra were measured on a Waters 70-SE-4F mass spectrometer. The synthesis of 1-azido-11-undecanethiol[1] (**2**) and lissamine rhodamine alkyne[2] (**7**) have been described elsewhere. Azide terminated SAMs on glass were prepared as published previously.[2]

Synthesis of Ferrocene Alkyne (5): 5-Hexyn-1-ol (1.410 mL, 13.04 mmol) and then dicyclohexylcarbodiimide (0.987 g, 4.78 mmol) were added to a solution of ferrocene carboxylic acid (1.001 g, 4.347 mmol), 4-dimethylaminopyridine (0.027 g, 0.217 mmol), and 4-(dimethylamino)-pyridinium *p*-toluenesulfonate (0.068 g, 0.217 mmol) dissolved in dry methylene chloride (45 mL) and the solution was stirred at ambient temperature under N_2 for 12 h. The crude reaction mixture was filtered through a pad of celite and the solvent evaporated. The crude product was subjected to chromatography (SiO_2, 1:9 EtOAc:Hexanes eluent) to give 0.990 g (73% yield) of **5** as an orange oil. **5**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 4.80–

4.78 (m, 2H, aryl -*H*), 4.38–4.36 (m, 2H, aryl -*H*), 4.23 (t, ^3J(H,H) = 6.4 Hz, 2H, CH_2O), 4.18 (s, 5H, aryl -*H*), 2.28 (dt, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 2.7 Hz, 2H, CH_2CCH), 1.98 (t, ^4J(H,H) = 2.7 Hz, 1H, CC*H*), 1.87–1.81 (m, 2H, CH_2), 1.72–1.65 (m, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): 171.7, 84.0, 71.4, 71.3, 70.2, 69.8, 68.9, 28.0, 25.2, 18.2; HRMS (ESI): Calcd for $C_{17}H_{18}FeO_2$ *m/z* = 310.0656, found *m/z* = 310.0649.

Synthesis of Pentafluorophenylether Alkyne (6): 1-Chloro-5-hexyne (1.57 mL, 16.3 mmol) was added to a slurry of pentafluorophenol (1.002 g, 5.433 mmol) and potassium carbonate (4.505 g, 32.60 mmol) in dry DMF (50 mL) and the mixture was stirred at 80 °C under N_2 for 16 h. The crude reaction mixture was partitioned between ethyl acetate (300 mL) and an aqueous solution of NH_4Cl (1M, 200 mL). The organic layer was washed with aqueous NH_4Cl (1M, 1 x 200 mL), H_2O (3 x 200 mL), and brine (1 x 200 mL) and then dried ($MgSO_4$) and evaporated. The excess 1-chloro-5-hexyne was distilled away (110 torr, 150 °C) and the residual crude product was subjected to chromatography (SiO_2, Hexanes eluent) to give 1.002 g (70% yield) of **6** as a colorless oil. **6**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 4.18 (t, ^3J(H,H) = 6.3 Hz, 2H, CH_2O), 2.28 (dt, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 2.7 Hz, 2H, CH_2CCH), 1.96 (t, ^4J(H,H) = 2.7 Hz, 1H, CC*H*), 1.93–1.87 (m, 2H, CH_2), 1.77–1.70 (m, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): 83.9, 75.3, 68.9, 28.9, 24.6, 18.1; ^{19}F NMR (377 MHz, $CDCl_3$, 25 °C, $CFCl_3$): δ –157.4 (d, ^3J(F,F) = 21.2 Hz, 2F, *o*-OCH_2), –163.9 (dd, ^3J(F,F) = 21.4, ^3J(F,F) = 21.4, 2F, *m*-OCH_2), -164.1 (t, ^3J(F,F) = 21.4, 1F, *p*-OCH_2); HRMS (FAB): Calcd for $[C_{12}H_9F_5O + H]^+$ *m/z* = 265.0652, found *m/z* = 265.0652.

Gold Substrates. Gold substrates were prepared by electron-beam evaporation of a titanium adhesion layer (15 nm, deposition rate of 1 Å/s) followed by gold (150 nm, deposition rate of 1 Å/s) onto 4 in. silicon(100) wafers in a cryogenically pumped deposition chamber. The silicon

wafers were cleaned prior to metal deposition for 10 minutes in piranha solution (1:3 30 wt % aqueous H_2O_2 : H_2SO_4; 130 °C), rinsed with deionized water, and dried under a filtered N_2 stream (**Warning**: Piranha solution reacts violently with organic material. It should be prepared freshly before use and disposed of properly. Do not store or combine with organic material.).

Formation of Mixed Azide Terminated SAMs on Gold. Method adapted from previously published source.[3] Freshly cleaved Au substrates were submerged in piranha solution (1:3 30 wt % aqueous H_2O_2 : H_2SO_4; 130 °C) for 1 min, rinsed with H_2O, submerged in concentrated HCl for 1 min, rinsed with copious amounts of H_2O followed by ethanol, and finally dried under a steam of filtered N_2. The cleaned gold substrates were then submerged in a deposition solution containing octanethiol (**1**, 0.5 mM) and 1-azido-undecanethiol (**2**, 0.5 mM) dissolved in ethanol (total concentration of thiol = 1 mM) for 16 h. After deposition the SAM substrates were rinsed with ethanol and dried under a stream of N_2.

PDMS Stamp Preparation.[4] A 10:1 (wt:wt) mixture of PDMS-Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp. Midland, MI) was poured over a fluoro-coated flat or patterned silicon wafer (SAM of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane, Gelest) in a Petri dish. The mixture was left at ambient temperature for 1 h before being placed in an oven at 60 °C for 16 h, after which the cured PDMS was slowly pulled away from the surface and cut into ~1 cm^2 squares to be used as elastomeric stamps. Stamps to be used for *Reagent-Stamping* were then oxidized in UV/ozone plasma (50 W, 10 seconds) and stored in water until just before use.

Metal-Coated PDMS Stamp Preparation. PDMS elastomer stamps were suspended in a cryogenically pumped deposition chamber and electron-beam evaporation of a titanium adhesion layer (10 nm, deposition rate of 1 Å/s) followed by Cu or Pt (50 nm, deposition rate of 1 Å/s)

was carried out. They were then cut into ~1 cm^2 squares to be used as elastomeric stamps either immediately after preparation or allowed to oxidize for at least 24 hours in air prior to use.

***StampCat* on Gold.** Ink solution (molecular alkyne, 5 mM in MeCN) was applied to the metallic side of a metal-coated PDMS stamp and the solvent allowed to evaporate, after which it was blown dry in a stream of N_2. The inked stamp was then brought into contact with the azide terminated SAM on gold substrate for 2 h with a load of 40 g to ensure conformal contact, after which the stamp was peeled away from the surface. The surface was then washed extensively with MeCN and EtOH, and then dried in a stream of N_2.

***StampCat* on Glass.** Ink solution (**7**, 1 mM in EtOH) was applied to the metallic side of a Cu-coated PDMS stamp and the solvent allowed to evaporate, after which it was blown dry in a stream of N_2. The inked stamp was then brought into contact with the azide terminated SAM on glass substrate for 1 min with a load of 40 g to ensure conformal contact, after which the stamp was peeled away from the surface. The surface was then washed extensively with EtOH and dried in a stream of N_2.

***Reagent-Stamping* on Gold.** To a freshly oxidized PDMS stamp was applied ink solution (molecular alkyne, 5 mM in MeCN) to cover the stamp surface followed by $Cu(OAc)_2$ (1 drop, 1 mM in EtOH) and ascorbic acid (1 drop, 1 mM in EtOH). The solutions were allowed to mix on the surface of the stamp for 1 min, blown dry in a stream of N_2, and brought into contact with the azide terminated SAM on gold substrate for 1 h with a load of 40 g to ensure conformal contact, after which the stamp was peeled away from the surface. The surface was then washed extensively with MeCN and EtOH, and then dried in a stream of N_2.

***Solution-Surface* Functionalization on Gold.** Method adapted from reported[1] procedure. A solution of **5** (3 mM), $CuSO_4 \bullet 5H_2O$ (1 mM), and ascorbic acid (2 mM) in DMF was placed on

top of azide-terminated SAM coated gold substrates. The reaction was performed protected from light under foil to prevent photo-oxidation of the thiol monolayers during the reaction. The substrates were rinsed extensively with EtOH, CH_2Cl_2, and H_2O after the desired reaction time had elapsed, and then dried in a stream of N_2.

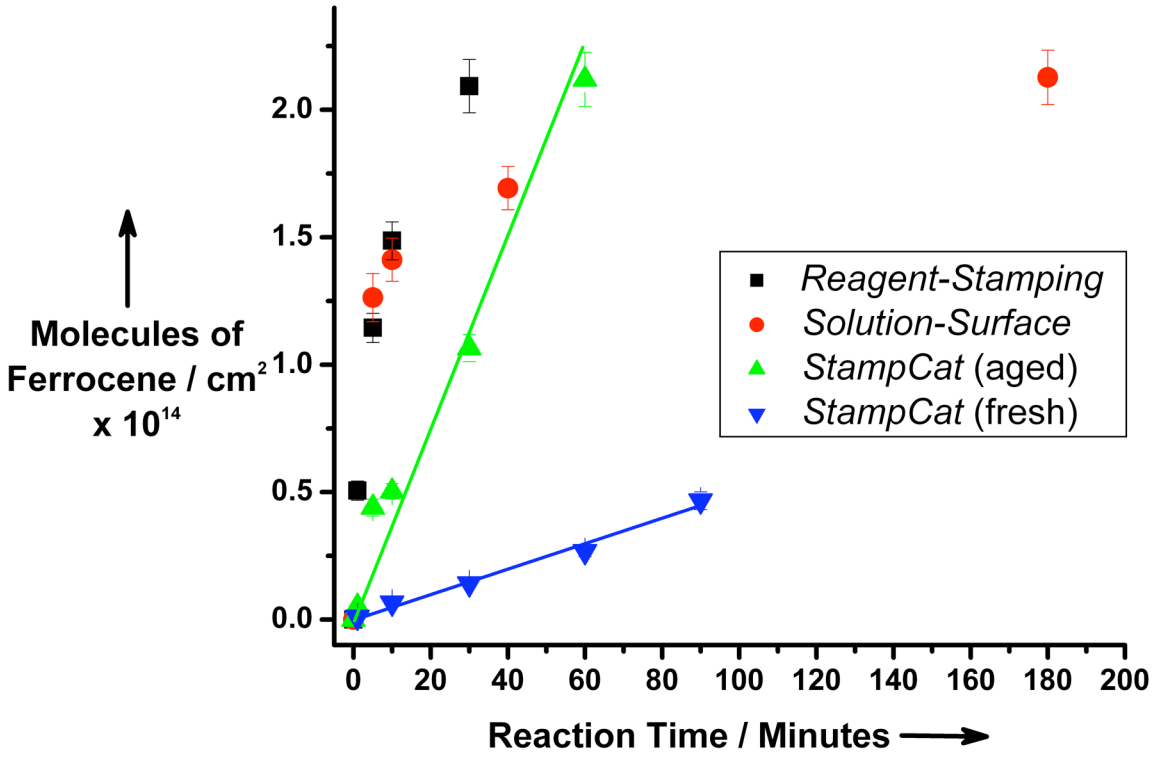

Figure S1. Replica of Figure 4b in the main text showing the full reaction time required for the completion of the *Solution-Surface* reaction.

***Solution* Reaction of 1-Azidohexane (3) and 1-Octyne (4).** 1-Azidohexane (**3**) (0.0050 g, 0.039 mmol) and 1-octyne (**4**) (0.0756 g, 0.786 mmol) were dissolved in DMF-d_7 (0.786 mL) in an NMR tube. Stock solutions of $CuSO_4 \bullet 5H_2O$ in DMF-d_7 (54 µL, 0.072 M, 0.1 eq. per azide) and ascorbic acid in DMF-d_7 (54 µL, 0.144 M, 0.20 eq. per azide) were added and the mixture left at RT. The reaction progress was monitored by comparing the integrated area of the disappearing $-CH_2N_3$ resonance at 3.47 ppm with that of the appearing $-CH_2N$(triazole) at 4.52 ppm in the ^{1}H NMR spectrum of the reaction mixture.

Electrochemical Measurements. Electrochemical measurements were performed in a custom built, cylindrically bored Teflon cone cell (10 mm inner diameter) pressed against the surface of the sample. The bored opening was filled with aqueous perchloric acid (1 M) as an electrolyte solution. The counter electrode (platinum coiled wire) and reference electrode (a glass frit-isolated Ag(s)/AgCl(s)/3 M NaCl(aq)) were each suspended in the electrolyte solution. The exposed surface extending from under the Teflon cone was contacted by a Tungsten probe (Micromanipulator Company, part number 7B) which served as the working electrode. The cell potential was controlled and the current generated was measured using a VMP Multi-Potentiostat (Princeton Applied Research, Oak Ridge, TN).

X-Ray Photoelectron Spectroscopy. X-Ray photoelectron spectroscopy (XPS) measurements were performed in an ultra high vacuum chamber of an M-probe surface spectrometer that has been described elsewhere.[5] All measurements were taken on the center of the sample at room temperature. Monochromatic Al K_α X-rays (1486.6 eV) were incident at 35° from the sample surface and a takeoff angle of 35° from the plane of the sample surface was employed to collected the emitted electrons. ESCA-2000 software was used to collect and analyze the data. Survey scans from 0 to 1000 eV were conducted followed by detailed scans for C 1s (282–292 eV), N 1s (393–410 eV), F 1s (680–696), and Fe 2p (700–730 eV).

Contact Angle Measurements. The sessile contact angle (θ) water were obtained with an NRL C.A. Goniometer Model #100-00 (Rame-Hart, Inc.) at room temperature. Contact angles were measured from sessile drops by lowering a 1 μL drop of H_2O from a syringe needle onto a surface and recording the contact angle at both edges of the drop. This was repeated three times and averaged to obtain the θ for the surface.

Contact angle measurements obtained from surfaces functionalized with ferrocenyl-alkyne **5** using each of the three methods suggested similar high levels of functionalization (Table S1). Surfaces functionalized with the pentafluorophenolate **6** using the *StampCat* technique were the most hydrophobic (80°). The contact angles for these functionalized surfaces differed from those for both the hydrophilic gold surfaces (56°) and the azide-containing mixed monolayers (77°), each of which is in agreement with previously recorded[1, 6] values. The similar contact angle changes for surfaces functionalized with **5** through each of the methods add qualitative support to the idea that all three procedures (Schemes 1b–d) proceed with comparable reaction efficiency.

Table S1: Contact angle goniometry for functionalized and unfunctionalized gold surfaces.

Surface	Method	Compound	H_2O Contact Angle (°)
Au	–[a]	–[a]	56.5 +/− 1.5
50% N_3 on Au	–[a]	–[a]	76.5 +/− 1.7
50% N_3 on Au	*Solution-Surface*	**5**	72.6 +/− 3.0
50% N_3 on Au	*Reagent-Stamping*	**5**	68.5 +/− 5.3
50% N_3 on Au	*StampCat*	**5**	73.5 +/− 3.4
50% N_3 on Au	*StampCat*	**6**	80.3 +/− 3.6

[a] No functionalization reaction was performed.

Infrared Surface Characterization. Surfaces were characterized by external reflection Fourier transform infrared spectroscopy using a Vertex 70 FT-IR spectrometer (Bruker Optics Inc.) equipped with a liquid N_2 cooled MCT detector and an AutoSeagull accessory (Harrick Scientific Products, Inc.). The light incident the sample was 86° from the normal and only p-polarized light was collected. A total of 128 scans were recorded with 4 cm^{-1} resolution. A background spectrum of a freshly cleaned gold substrate was subtracted from the spectra were baseline corrected using the concave rubberband method (25 iterations, excluding CO_2 bands, 256 baseline points).

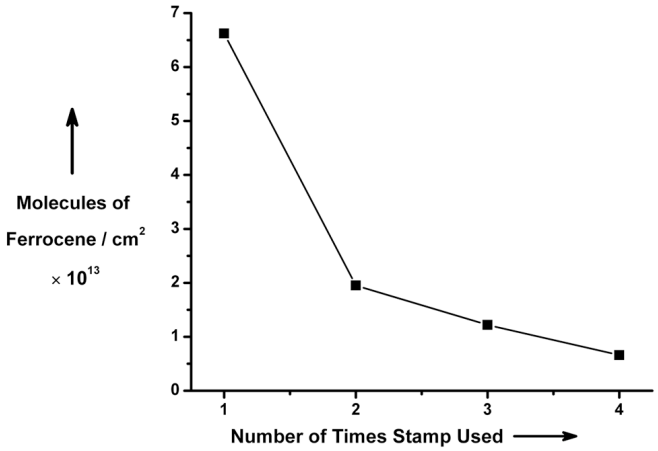

Figure S2. Electrochemically-determined ferrocene coverage as a function of repeated stamp use for the *StampCat* method.

Atomic Force Microscopy (AFM) Imaging. AFM measurements were carried out with a digital multimode Nanoscope III (Digital Instruments, Santa Barbara, CA, USA) scanning force microscope in contact mode, with 512 x 512 data acquisitions, using V-shaped Si_3N_4 AFM tips (Nanoprobes, Digital Instruments) with a nominal spring constant of 0.32 N/m. The scan angle was set to 90º. Typical scan rates of 1-2 Hz were used to acquire the data. All imaging was conducted at room temperature in air.

Laser Scanning Confocal Microscopy/Optical Microscopy. Fluorescence images were obtained on Carl Zeiss LSM 510 with an excitation Ar-Kr laser beam of 563 nm wavelength and a 40 x objective. The emitted fluorescence was collected on a PMT Hamamatsu R6357 spectrophotometer. All imaging was conducted at room temperature in air.

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